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Geospatial statistics elucidate competing geological controls on natural CO_2 seeps in Italy

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ABSTRACT

Site selection for the geological storage of CO_2 for long timespans requires an understanding of the controls on containment, migration and surface seepage of subsurface CO_2 fluids. Evidence of natural CO_2 migration from depth to surface is documented at 270 sites from Italy, a prolific CO_2 province. Previous studies indicate that CO_2 delivery to and from buried structures that host CO_2 accumulations is fault controlled, but that competing controls on the CO_2 flow pathways affect the location and style of CO_2 release. Here, we conduct a meta-analysis using a novel geospatial approach to statistically determine the relationship between geological setting and structures and the CO_2 seep spatial distribution and characteristics (morphological type, flux and temperature) in central Italy. We find that seep distribution differs on two spatial scales corresponding to geological setting. On large scales (>5 km) seeps are isotropically distributed and align with regional structures such as anticlines, decollements, and extensional faults. On local scales (<5 km) seeps cluster and align with subsidiary geologic structures, including faults and lithological boundaries. The detailed location and flux of seeps within clusters is influenced by regional structural domain: in the Tyrrhenian seeps tend to be located along fault traces; whereas seeps are located as springs in tip and ramp regions of fault scarps in the Apennines. Thus, our geospatial approach evidences, at a regional scale, how macro-crustal fluid flow is governed by deep extensional and compressional features, but, once CO_2 reaches shallower structures, how smaller-scale features and hydrogeological factors distribute the CO_2 fluids in the near-surface, dependent on the geological setting. This work not only demonstrates useful application of a novel geospatial approach to characterize competing crustal controls on CO_2 flow at different scales, but also informs the design of appropriate site characterization and surface monitoring programs at engineered carbon stores.

Keywords: CO_2 seeps; crustal fluid flow; CO_2 storage; geographical information systems (GIS); site characterization; Italy.

INTRODUCTION

Carbon Capture and geological Storage (CCS) can significantly reduce anthropogenic CO_2 emissions from large industrial sources of CO_2 (IPCC, 2005; Scott et al., 2012). However for CCS to contribute effectively to climate change mitigation, the CO_2 must remain in the subsurface for tens of thousands of years (IPCC, 2005; Shaffer, 2010). Examining naturally-occurring CO_2 seeps allows quantitative examination of the diverse crustal pathways taken by CO_2 migrating from depth (Burnside et al., 2013; Gal et al., 2012; Miocic et al., 2016; Pearce et al., 1996), and thus guides the selection of secure storage sites, and the robust design of low-cost monitoring programs capable of detecting potential leakage to surface. Further, understanding of CO_2 flow pathways not only informs leak prevention, but also leak remediation (IEA GHG, 2007).

Natural CO_2 seepage is widespread in Italy (Minissale, 2004), where 308 CO_2 seeps at 270 locations exhibit a variety of surface expressions ('types'), temperatures and fluxes (Chiodini et al., 2008). These seeps have already proven valuable for studying the environmental and social impact of CO_2 escape (Beaubien et al., 2008; Roberts et al., 2011), storage site monitoring techniques (Bateson et al., 2008) and CO_2 leak pathways (Roberts et al., 2017; Trippetta et al., 2013).

The location of subaerial CO_2 seeps in Italy are shown in Figure 1, along with major structural features. These structures are mostly derived from tectonic processes associated with the subduction of the Adria plate beneath the European margin (Cosentino et al., 2010; Ghisetti and Vezzani, 2002). Initiating in the Miocene, NE-SW compression caused tectonic stacking of Mesozoic-Tertiary carbonate platform and foredeep sediments which concentrated in a NE migrating thrust belt. Coeval back-arc extension thinned the crust in the Tyrrhenian sector, leading to high heat flow and active volcanism since the Pliocene and developing distinct NW-SE trending structural domains shown in Figure 1; the thinned Tyrrhenian back arc, the thrust belt, and the thickened Adriatic foredeep.

CO_2 seep distribution and flux concentrates in the peri-Tyrrhenian (Chiodini et al., 2004) and decreases towards the Apennines, where modern day seismicity concentrates. Few seeps occur towards the foredeep. Individual seep CO_2 fluxes range from < 1 to > 2000 tonnes/day (t/d) (Chiodini et al., 2010), but 10-100 t/d is most common (Chiodini et al., 2008; Roberts et al., 2011). Overall non-volcanic diffuse regional CO_2 release from central and southern Italy is globally significant (Ascione et al., 2018; Chiodini et al., 2017). Studies find that seeping CO_2 may have a mixture of origins (Ascione et al., 2018; Minissale, 2004), but the largest component derives from deep degassing from a mantle contaminated with subducted crustal carbonates (Chiodini et al., 2011; Gambardella et al., 2004; Italiano et al., 2009; Minissale, 2004).

[Fig 1]

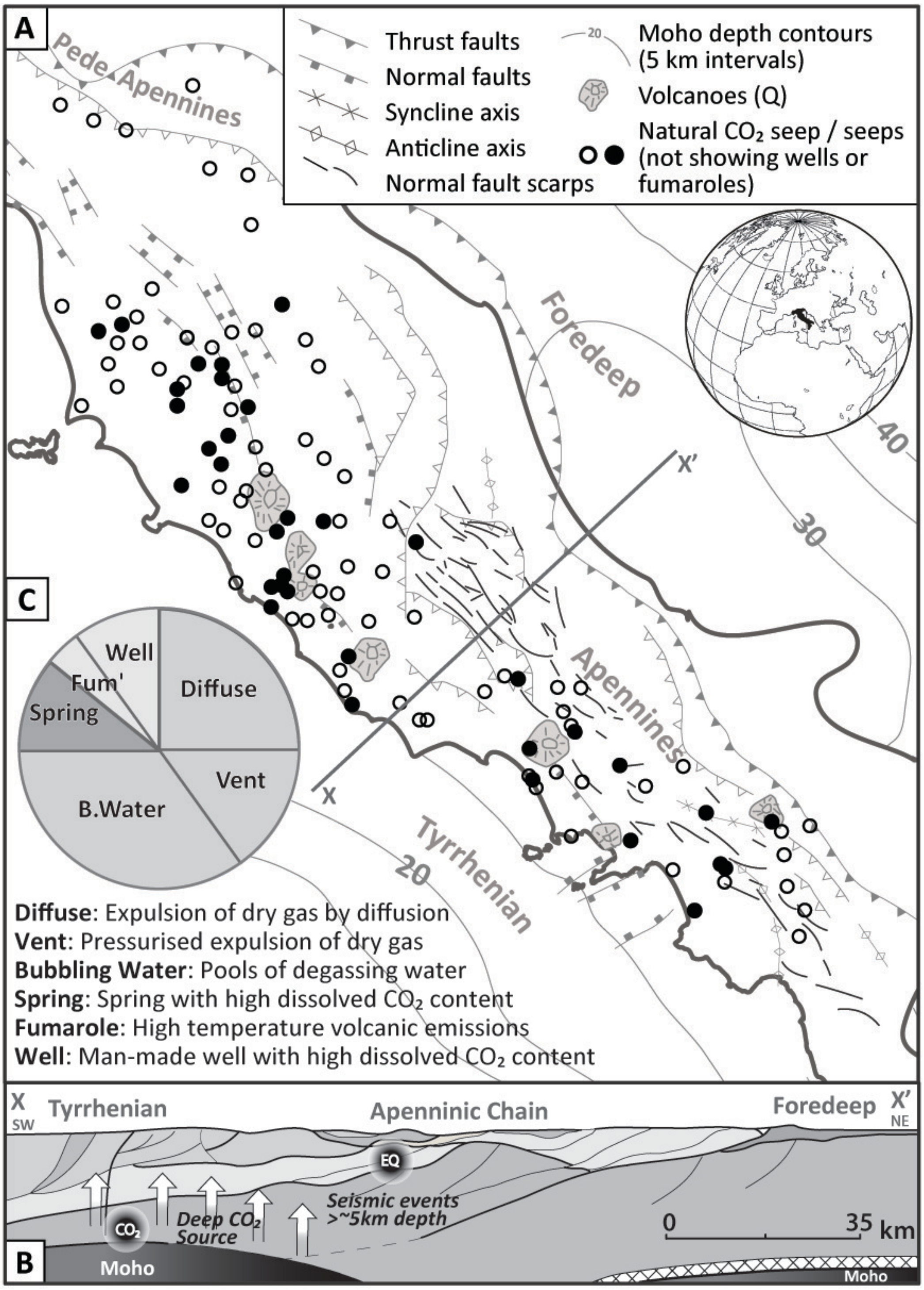

Fig 1. Schematic map of Italy showing the location of regional geological structures and Quaternary (Q) volcanoes (adapted from Brozzetti, 2011; Patacca et al., 2008), CO_2 seeps (Chiodini et al., 2008) (where filled symbols indicate multiple seeps), Moho depth contours (Di Stefano, 2011) and mapped normal fault scarps after (Roberts, 2008). Filled symbols show multiple seeps. Location of Italy shown on globe inset. (b): Crustal cross-section of the central Apennines modified from (Calabro et al., 2003; Ghisetti and Vezzani, 2002; Improta et al., 2003). While earthquakes (EQ) and CO_2 delivery occur across the section, circles indicate the main, simplified, occurrences. (c): Proportion of CO_2 seep types classified qualitatively according to surface expression.

Numerous studies of seep systems in Italy have highlighted the role of buried geological structures in Mesozoic carbonates on CO_2 accumulation and leakage to surface. These include shallow (~1 km) or deep (~ 5 km) anticlines (Bicocchi et al., 2013; Chiodini et al., 2010; Roberts et al., 2017) and horsts (Carapezza and Tarchini, 2007), but CO_2 accumlations also occur in shallow pockets within Pleistocene sands (Barberi et al., 2007; Bigi et al., 2014). CO_2 delivery to and from these structures tends to be fault associated (Agosta et al., 2008; Annunziatellis et al., 2008; Ghisetti et al., 2001). Indeed, buried faults have been be identified from CO_2 or Radon gas anomalies in Pleistocene cover (Bigi et al., 2014; Ciotoli et al., 2015; Etiope et al., 2005). At depth, CO_2 is known to affect fault properties (Collettini et al., 2008; Collettini and Holdsworth, 2004; Smith et al., 2008) and seismogenesis (Bonini, 2009a; Chiodini et al., 2004; Collettini and Barchi, 2002; Di Luccio et al., 2018; Malagnini et al., 2012; Miller et al., 2004) in Italy. Seismic events are observed to affect CO_2 seep flux and style (Bonini, 2009b; Heinicke et al., 2006). While fault affect crustal fluid flow by different mechanisms (Choi et al., 2016; Faulkner et al., 2010), and offer important barriers or conduits for CO_2 flow in the subsurface, along-strike permeability of faults is highly variable (Curewitz and Karson, 1997; Faulkner et al., 2010), and towards the surface, many other factors influence local gas flow pathways, including topographic and hydrological factors (Roberts et al., 2014) and vadose zone properties (Annunziatellis et al., 2008; Roberts and Stalker, 2017). As such, CO_2 fluid pathways are affected by competing crustal controls, from regional geological structures km's deep to top soil composition.

While several regional and sub-regional studies of CO_2 seep occurrences are reported (Chiodini et al., 1995; Frondini et al., 2008), the dominant controls on CO_2 seepage have not yet been systematically studied across a range of scales and geological settings. Here we address this gap. We adopt a novel macroscopic approach to illuminate the competing crustal controls on natural CO_2 fluid pathways by applying a novel geospatial statistical approach, the two-point spatial correlation function, to a database of CO_2 seep characteristics integrated with geological data from central Italy. The two-point spatial correlation function is a technique developed for cosmology (Peebles, 1980), and previously used in earth science only to investigate earthquake aftershock distributions (Richards-Dinger et al., 2010). The method quantifies the departure from homogeneity of point data, allowing the point distributions and orientations to be examined at a range of scales. As such, we do not examine each seep, cluster of seeps, or region of degassing on a case by case basis; given that these have been the subject of numerous previous studies. Rather, we focus on using the rich geospatial dataset of CO_2 seepage in Italy to explore whether geospatial statistics can elucidate the geological controls on seep location, distribution, and characteristics over the entire region of central Italy.

METHODS

The database of CO_2 seeps (Chiodini et al., 2008) quantifies seep location, morphological type, flux and temperature (where data are available). We do not consider wells (boreholes known to leak CO_2) or fumaroles in our analyses since man-made and volcanic seeps are not representative of leakage from geological CO_2 stores. The remaining seep data are analyzed together with geological structures and geological boundaries in mainland Italy, including 1:1M and 1:100k scale geological maps (ISPRA, 2010) (in this dataset, only the location of the fault trace is known; there is no information on fault characteristics, such as type, throw, age), normal fault scarps in the Apennines (Roberts, 2008), seismic events, and subsurface carbonate structures (Nicolai and Gambini, 2007).

For more detail on these data see SI Methods. A synthetic Poisson (random) point distribution is used as a ‘control’ to compare against the seep data. The synthetic points are distributed within the areal extent of mainland Italy. A second Poisson distribution is created with the areal extent the Tyrrhenian, since most seeps are located in this region (see SI Methods).

We used two approaches to test the scale-dependence of point spatial relationships:

(1) Proximity analyses determined the distance and azimuth of seeps to the nearest surface trace of a fault or lithological contact. We used the built in ArcGIS proximity analysis tool to find the point on a fault line that is the shortest distance from a seep, and then take the distance and azimuth between the seep and that point of the fault. This tells us how far the nearest fault is from each seep, and where the seep is in relation to that fault.

(2) Point clustering was first examined using standard GIS tools (see SI Methods) then analyzed more sophisticatedly using the two-point spatial correlation function. The two-point correlation method quantifies the departure from homogeneity of a distribution of points. The correlation function is expressed as the probability of finding a pair of points within an area, and is usually explored over an area of incrementally increasing radius. The correlation function plots as a power law, $P \propto r^{\kappa}$, where P is probability, r is radius, and the constant κ describes the spatial distribution: for randomly distributed points, $\kappa = 2$; for clustered points, $k<2$; for points randomly distributed on a line, $\kappa = 1$. The distribution of azimuths between pairs of points can also be measured by this technique. Any change in point azimuths over increasing area of study indicates anisotropy in the point distribution (i.e. whether and how the location of points in relation to each other changes as the area of study increases).

RESULTS

Seep Spatial Distributions

Two-point correlation function for seep and synthetic data (Fig 2a) shows that separation distances control distribution:

i) Between ~5 - ~100 km the correlation function is the same for seep and synthetic data and $\kappa = 2$, indicating these points are isotropically distributed. The roll-off at distances greater than 100 km is a finite size (censoring) effect (Bonnet et al., 2001) from the spatial extent of Italy and is less notable in the synthetic data because points are distributed across the width of Italy whereas seepage focusses west of the Apennines. Indeed, roll-off is similar for synthetic and seep when the synthetic points are distributed only in the Tyrrhenian (see SI Fig 3).
ii) At separation distances of <~5 km, κ decreases to ~0.5-1, indicating non-random spatial clustering ($\kappa = 1$ indicates seeps are aligned, and synthetic data κ remains ~2).”

The distribution of azimuths between all pairs of seeps and synthetic points is separated above and below 10 km, the distance where the κ function begins to change (Figs. 2b, c). At separation distances < 10 km seeps show several orientations approximately 30-40° apart. Synthetic data show peaks that relate to few point pairs rather than a preferred orientation. Above 10 km, seep pairs show a preferred NW-SE (140-160°) orientation which synthetic data does not exhibit. Spatial relationships are unaffected by outcrop shape/extent or seep density (see SI Results, SI Fig 3).

CO_2 seeps in mainland Italy are significantly clustered (99.9% confidence) compared to a spatially random process and form small clusters (<5 km width) that occur ~20 km apart (see SI Fig 2). When analyzed by seep type, only springs are not significantly clustered (see SI table 1).

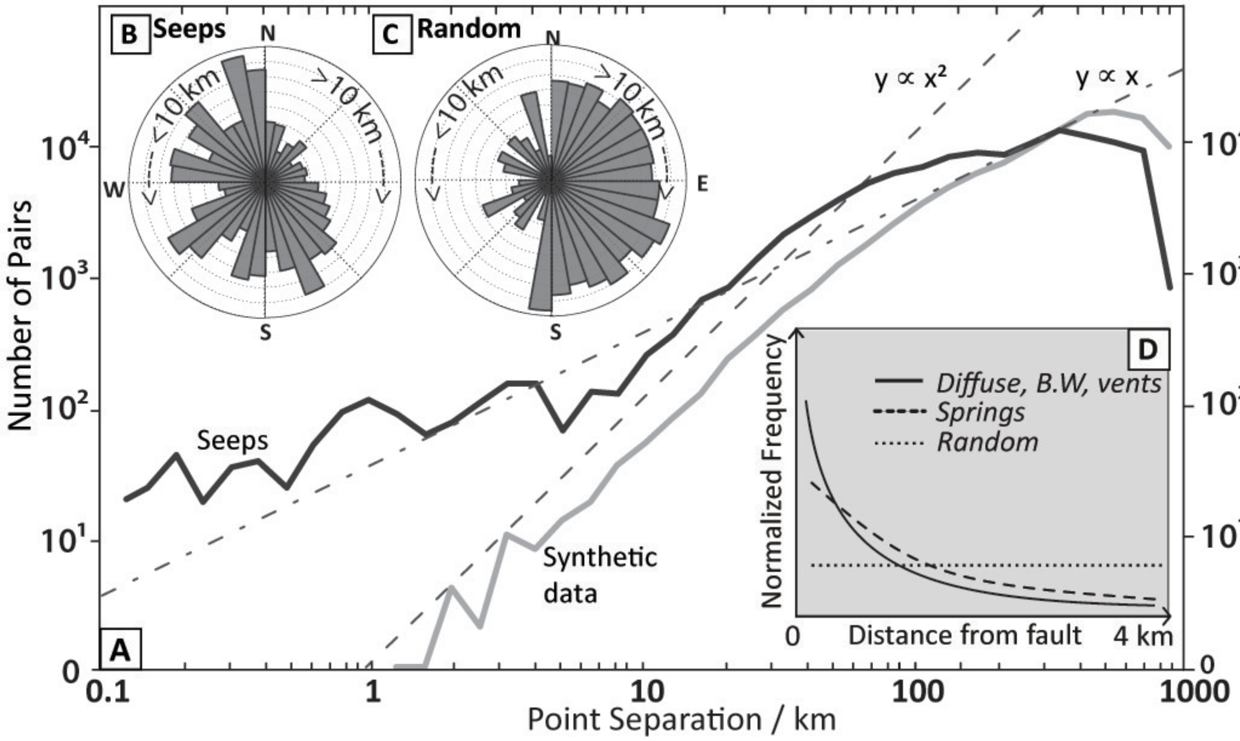

Figure 2(a): Point-distance correlation functions for seep and synthetic (random) data in mainland Italy, showing the break in slope for seep data around ~5 km, and roll-off towards ~100 km in both datasets. The synthetic dataset is not clustered so few pairs are <10 km apart. Inset shows distribution of azimuths for points <10 km (anticlockwise) and >10 km (clockwise) for (b) seeps, and (c) synthetic data. Seeps show several favored orientations <10 km and NW-SE trend >10 km separation. (d) Normalized line histogram of seep types and distances from lithological boundaries and faults. B.W refers to bubbling water seeps.

Role of Geological Structures

Seeps spatially occur close to faults (Fig 2d), and all seep types are exponentially more common closer to fault traces except springs which show a much weaker, near-linear, increase. Although the resolution of the fault populations limits the confidence of spatial interrogation at distances <1 km, 90% of vent, diffuse and bubbling water seeps are located <1 km, increasing to 2 km for springs. These relationships are consistent for both geological datasets (1M, 100k). Seep-fault azimuths are principally SW (-NE).

Seeps are also preferentially located towards lithological boundaries; 76% of all seeps and all CO_2 springs are located < 1 km from lithological boundaries for both geological datasets (Fig 2d and 3a). Seeps show no favored orientation from lithological contacts, unlike faults. Seep flux and temperature datasets are incomplete, but neither correlate with proximity to faults or lithological contacts.

Known seeps occur above structural highs of Mesozoic carbonate subsurface topography. For example, two CO_2 seeps occur above an anticline crest known to host CO_2 (Chiodini et al., 2007;

Chiodini et al., 2010), and others appear near to the crest, or local highs on the flanks, of carbonate structures and décollements (Fig 3b).

In the seismically-active Apennines, seeps are rarely located along fault scarps. The few (37) CO_2 seeps which are located <10 km of a fault scarp are mostly (70%) springs with high fluxes (all but one seep with quantified flux emit >10 t/d). Unlike seeps towards the Tyrrhenian, Apennine seeps are located SSE of faults and typically positioned toward the fault tip or in ramp structures in fault step-over zones (Fig 3c).

[Fig 3]

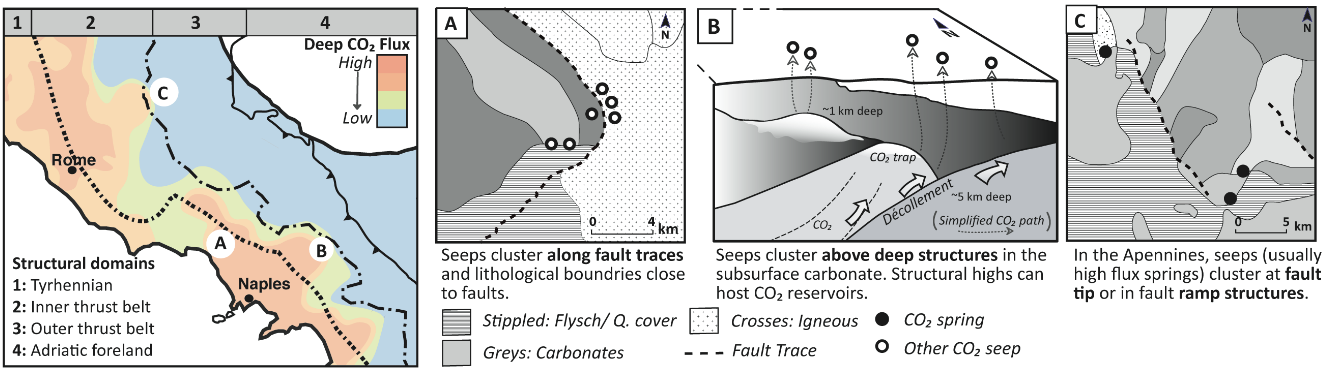

Figure 3: Map of central Italy showing CO_2 seepage in the major structural domains (Ghisetti and Vezzani, 2002), distribution of deep CO_2 flux (Chiodini et al., 2004), and the location of three examples illustrating the range of structural controls on CO_2 seeps within the three domains of degassing. The specific lithologies in (a) and (c) are not indicated here, but can be found from (ISPRA, 2010). The three scenarios are not mutually exclusive.

A) *Major and minor fault traces*. Near Suio in Castelforte (Lazio), where 4 bubbling water and 2 vent seeps located along, or close to, fault traces and lithological boundaries in 1:1M and 1:100k geological datasets (ISPRA, 2010) which do not specify the fault types.

B) *Leakage from subsurface structures*. Close to Rocca San Felice in Avellino (Campania), where 2 CO_2 vents are located above the Monte Forcuso anticline that is known to host CO_2 reservoir.

C) *Fluid flow at fault tip points*. East side of Rieti basin (Lazio) where 3 springs (2 high, 1 very high flux) emerge towards the fault tip points of a normal fault scarp, rather than along the fault trace. The scarp was mapped in detail by (Roberts, 2008) (shown in the image).

DISCUSSION

Subsurface plumbing of CO_2 fluids

Seeps are preferentially located near to faults and show several preferred point pair azimuths within clusters (Fig 2). Regional NW-SE structures may be a primary control on CO_2 seepage, but towards the surface it seems that any fault (i.e. any range of orientation) is the secondary control that governs where seeps emerge within a cluster. Fault orientations are more varied in the 1:100k dataset than the 1:1M (see SI results). So as well as subsidiary faults and fractures, which can exhibit a wide range of orientations to the primary deformation structure there are also structures which pre-date the Miocene compression and extension (Bigi and Costa Pisani, 2005). CO_2 migrating from buried anticline or horst structures may do so via whichever of these features provide transmissive pathways.

As observed by previous authors, our analyses find that geological structures determine the presence and location of CO_2 seeps in Italy. We also observe that distance from a fault influences the seep type (Fig 2d). Seep type may therefore indicate the degree of near-surface spread from geological structures, and therefore the relative control of other geological and hydrological factors other than the fault trace (Roberts et al., 2014). For example, compared with other seep types, the location of CO_2 springs shows the weakest relationship with faults and the strongest relationship with lithological boundaries. It is not surprising that crustal migration pathways of aqueous CO_2 fluids differ from gaseous or free phase CO_2. The location of CO_2 springs is controlled by the hydrogeological characteristics of the aquifers. Assuming the aquifer is well mixed, external CO_2 could have entered the aquifer at any point(s) within the aquifer subsurface extent, in which case CO_2 rich springs do not indicate the location of CO_2 fluid flow pathways from depth i.e. the spring may be located far from the fault trace(s) supplying the CO_2.

The robustness of our results is of course limited by the resolution of the geological data and the completeness of the gas seep information. However, our meta-analysis identifies three different seep settings in central Italy (Fig 3). These settings are distinct, but are not mutually exclusive, and align with current understanding of crustal controls on fluid flow.

1. *Major and minor fault traces*. In the Tyrrhenian, the extended back-arc region, 90% of vent, bubbling water and diffuse seeps are located within 1 km of a fault (Fig 3a). The location of seeps suggests that in this geological setting CO_2 fluids are channeled by barrier/conduit properties of the fault wall and so seeps emerge along it, close to fault traces.

2. *Leakage from subsurface structures*. In many cases, deep geological structures supply CO_2 to surface seeps. As such, due the structural trend of compression and extension structures in central Italy the resulting seep clusters supplied by buried CO_2 accumulations will be located NW-SE of each other (Fig 3b). The orientation of faults related to, or pre-or post- dating these subsurface structures are likely to be responsible for the leakage of CO_2 to surface. For example, at Mefite D'Ansanto, the example in Fig 3b, observed polarization of ambient seismic noise may indicate the presence of faults governing gas escape from the Monte Forcuso CO_2 reservoir (Pischiutta et al., 2013).

3. *Fluid flow at fault tip points*. There are fewer CO_2 seeps located within the Apennines compared to the Tyrrhenian sector, and Apennine seeps tend to be springs with high fluxes and occur at lithological boundaries (Fig 3c). This indicates that there are limited pathways to surface for free-phase CO_2 fluids in this region, which is also the most seismically active part of central Italy. Instead, CO_2 from depth enters aquifers, and its emergence as CO_2 springs is then controlled by hydrogeology. We find that springs tend to emerge close to fault tips or in ramp structures in step-over zones. While these fault scarps are clearly an important control on crustal fluid flow in the Apennines, it is not necessarily the case that fault tips or ramp structures in step-over zones offer pathways for CO_2 migrating all the way from depth to surface.

We propose that orientation of regional geological structures leads to the observed surface distribution of seep clusters in central Italy (Fig 2). Extensional faults of the Apennines and major normal faults in the Tyrrhenian sector align NW-SE (see SI Results), and although compressional structures are more variable in their orientation, these are also predominantly NW-SE in central

Italy, where CO_2 degassing concentrates. This means that our analyses cannot distinguish which fault types exert greatest control on CO_2 seep distributions and characteristics. Ghisetti et al. (2001) found that extension-related structures in Italy permit fluid flow during deformation, whereas contraction-related structures were initially closed but opened during subsequent exhumation and extension. Regional extensional and compressional features in Italy may therefore be important for governing crustal fluid flow, supplying deep-derived CO_2 to buried structures within the tectonized Mesozoic carbonates, and ultimately to seep clusters (Fig 3b). However, at a global scale, Tamburello et al. (2018) have shown that there is a spatial correlation between CO_2 discharges and the presence of active fault systems, and particularly with normal slip faulting.

Implications for Carbon Capture and Storage

Understanding the geological controls on CO_2 fluid flow can aid the prevention of leakage from engineered CO_2 stores by informing effective site selection criteria. Moreover, should unintended leakage to surface occur, understanding the geological controls on CO_2 fluid flow can inform the assessment of the potential CO_2 seep locations and characteristics.

In Italy, we observe that CO_2 seepage is clustered, and that the location, distribution, and type of seepage within and between these clusters are controlled by a number of factors. These include, in order of importance (as highlighted by our study) the orientation of regional structures, the geological setting, the density and orientation of local geological structures, and whether CO_2 is migrating in spring water or as a separate phase. It is therefore important to characterize not only the storage formation and overburden, but to consider the storage system in the context of the geological setting and near-surface geology.

Our work contributes towards predictive models of CO_2 leak pathways. These models are important to de-risk sites selected for engineered storage, since site selection protocols can minimize risk of leakage (Miocic et al., 2016). Further, whether CO_2 migrates and/or is emitted to surface as gas or as a dissolved constituent of springs has implications for the environmental and social risk and impact of CO_2 leakage (Roberts et al., 2011; Lemieux, 2011; Jones et al., 2015), and so the design of robust and cost-effective monitoring programs to detect CO_2 migrating to surface should CO_2 migrate from its primary storage formation (Jenkins et al., 2015).

Author Contributions

J. J. Roberts designed the research, conducted the data analysis and wrote the paper. A. F. Bell contributed to research design and data analysis, and R. A. Wood, and R. S. Haszeldine contributed towards the research design and writing of this paper.

Competing Financial Interests

There are no conflicts of interest to declare.

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Data availability statement

The analyses presented in the paper used publicly available datasets, as specified in the article text and the SI Methods.

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